

IAP20 Rec'd PCT/PTO 30 DEC 2005

SILICONE COMPOSITION WHICH CAN BE CROSSLINKED BY MEANS  
OF DEHYDROGENATIVE CONDENSATION IN THE PRESENCE OF A  
METAL CATALYST

The present invention relates to silicone  
5 compositions which can be crosslinked by  
dehydrogenative condensation between reactive  $\equiv\text{SiH}$  and  
 $\equiv\text{SiOH}$  units and which employ an iridium complex as  
catalyst. It also relates to a preparation process  
relating thereto, to the crosslinked materials thus  
10 obtained and to the articles coated with or composed of  
these materials.

The invention thus relates to the field of the  
catalysis of dehydrogenative condensation reactions  
which make possible silicone polymerization/cross-  
15 linking. The reactive entities involved are monomers,  
oligomers and/or polymers of polyorganosiloxane (POS)  
nature.

The reactive units concerned in these entities  
are, on the one hand, the  $\equiv\text{SiH}$  units and, on the other  
20 hand, the  $\equiv\text{SiOH}$  units. Dehydrogenative condensation  
between these silicone reactive units and entities  
results in the formation of  $\equiv\text{Si-O-Si}\equiv$  bonds and in the  
release of hydrogen gas. This dehydrogenative  
condensation is an alternative to the polymerization/  
25 crosslinking routes known in the field of silicones,  
namely the  $\equiv\text{SiH}/\equiv\text{Si-alkenyl}$  (vinyl) polyaddition route  
and the  $\equiv\text{SiOR}/\equiv\text{SiOR}$  (with  $\text{R} = \text{alkyl}$ ) polycondensation  
route. All these polymerization/crosslinking routes  
result in more or less polymerized and more or less  
30 crosslinked silicone products which can constitute  
products usable in multiple applications: adhesives,  
leaktightness products, pointing products, adhesion  
finishes, release coatings, foams, and the like.

The applications more particularly targeted by the  
35 invention are crosslinked silicone elastomer coatings  
of use as release coatings on various solid supports,  
for example flexible fibrous supports (made of paper or  
fabric, e.g.) or flexible nonfibrous supports, such as  
polymer films (polyester or polyolefin, e.g.) or

alternatively supports made of aluminum or of any other metal, such as tin plate.

Another application to which the invention more especially relates is targeted at crosslinked silicone  
5 foams.

The dehydrogenative condensation reaction involves metal catalysts based on platinum, rhodium, palladium, ruthenium, boron or iridium, platinum catalysts being the most common (FR-B-1 209 131, US-B-4 262 107, EP-A-  
10 1 167 424 and FR-A-2 806 930).

FR-B-1 209 131 discloses in particular the reaction between a silanol  $\text{Ph}_2\text{Si}(\text{OH})_2$  and a diorgano-siloxane  $[(\text{Me}_2\text{HSi})_2\text{O}]$ , with Me = methyl and Ph = phenyl, by dehydrogenative condensation in the presence of  
15 chloroplatinic acid ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ), which results in a polydiorganosiloxane possessing a D unit,  $-\text{R}_2\text{SiO}_{2/2}-$ , of dimethyl or diphenyl type. This reaction produces a rapid evolution of hydrogen.

US-B-4 262 107 relates to a silicone composition  
20 of polyorganosiloxane (POS) type comprising more specifically a polydimethyldisiloxane possessing silanol ends and a crosslinking agent composed of a POS possessing  $\equiv\text{SiH}$  units in the chain and possessing trimethylsilyl ends, a catalyst composed of a rhodium  
25 complex  $(\text{RhCl}_3[(\text{C}_8\text{H}_{17})_2\text{S}]_3)$ , and a crosslinking inhibitor (for example, diethyl maleate, diethyl acetylenedicarboxylate, triallyl isocyanurate or vinyl acetate).

EP-A-1 167 424 and US-A-2002/0013441 disclose the production of linear block silicone copolymers by  
30 dehydrogenative condensation of POS polymers possessing silanol ends and of aromatic POS possessing  $\equiv\text{SiH}$  ends in the presence of a metal catalyst. Hydrosilylation catalysts are suitable and it is possible to employ the metals platinum, rhodium, palladium, ruthenium and  
35 iridium, preferably platinum, and compounds of these metals. The hydrosilylation catalyst is in particular a platinum complex, such as the Karstedt catalyst.

FR-A-2 806 930 relates to the use of boron derivatives of tris(pentafluorophenyl)borane type.

It would be of great usefulness to have available a broader panel of dehydrogenative condensation catalysts and in particular of catalysts which make it possible to optimize the kinetics of the reaction and the concentration/effectiveness of the catalyst ratio.  
5 An object of the invention is thus to provide novel dehydrogenative condensation catalysts which are particularly effective.

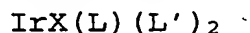
Another object of the invention is to provide  
10 catalysts with a lower cost price than platinum catalysts.

Another object of the invention is to provide a panel of catalysts which are easy to prepare, so as to more readily present the catalyst which is the best  
15 suited to such and such a reaction and/or under such and such operating conditions.

Another object of the invention is to provide catalysts having moderate activation temperatures (mobilization of a small amount of energy for the  
20 catalysis of the dehydrogenative condensation:  $\theta^{\circ}\text{C}$   $< 150^{\circ}\text{C}$ ) and/or making possible better control of the evolution of hydrogen gas and of the quality of the polymerized product and/or of the crosslinked network, and/or, finally, making it possible to limit the side  
25 reactions.

Another essential object of the present invention is to provide  $\equiv\text{SiH}/\equiv\text{SiOH}$  silicone compositions which can be polymerized or crosslinked by dehydrogenative condensation in the presence of such a catalyst.

30 Patent application PCT/FR02/01340, filed on 18 April 2002 (and unpublished at the date of filing of the present application), discloses silicone compositions which crosslink by dehydrogenative condensation and which use, as catalyst, an iridium  
35 complex corresponding to the following formula (I'):



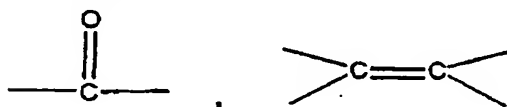
in which:

- o Ir is an iridium atom of valency I or III,
- o X represents a one-electron ligand,

preferably chosen from the group consisting of halogens, hydrogen, an acetate, a substituted or unsubstituted aromatic or heteroaromatic group, CN, RO, RS, R<sub>2</sub>N or R<sub>2</sub>P with R corresponding to an alkyl, aryl or arylalkyl unit,

o L and L' independently represent a two-electron ligand, preferably chosen from the group consisting of:

- hydrocarbon radicals comprising at least one unit:



- the radicals:

-PR'<sub>3</sub>, -P(OR')<sub>3</sub>, R'<sub>2</sub>O, R'<sub>2</sub>S, R'<sub>3</sub>N and =CR'<sub>2</sub>

with R' independently representing a substituted or unsubstituted aromatic or heteroaromatic group or alternatively an alkyl, aryl or arylalkyl radical,

- C<sub>n</sub>H<sub>n+1</sub>- (with n a positive natural integer), preferably corresponding to C<sub>6</sub>H<sub>5</sub>-.

This patent application PCT/FR02/01340 cites in particular Vaska's complex IrCl(CO)(triphenylphosphine)<sub>2</sub>.

The objects set out above, and others, are achieved by the present invention, which relates first of all to a silicone composition which can be crosslinked by dehydrogenative condensation, this composition comprising:

o -A- at least one organosiloxane monomer, oligomer and/or polymer having, per molecule, at least one reactive =SiH unit;

o -B- at least one organosiloxane monomer, oligomer and/or polymer exhibiting, per molecule, at least one reactive =SiOH unit;

- o -C- at least one catalytic complex;
- o -D- optionally at least one crosslinking inhibitor or retarder;
- o -E- optionally at least one polyorgano-  
5 siloxane (POS) resin;
- o -F- optionally at least one filler;

characterized in that the catalytic complex -C- is an iridium complex obtained by reacting together:

-Cl-, on the one hand, an iridium complex of  
10 formula (I):



in which:

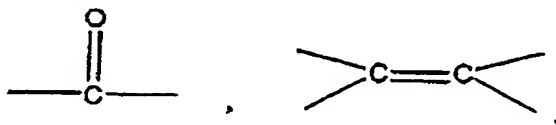
1/ n is 1 or 2 and:

- (a) if n is 1,  $\Sigma$  is a 3-electron radical ligand  
15 LX (according to the definition given in the work "Chimie Organométallique" [Organo-metallic Chemistry] by Didier Astruc, published in 2000 by EDP sciences, cf. in particular Chapter 1, "Les complexes mono-  
20 métalliques" [Monometallic Complexes], pages 31 et seq.), in particular a ligand derived from acetylacetone, from a  $\beta$ -keto ester, from a malonic ester, from an allyl compound, from a carbamate, from a dithio-  
25 carbamate or from a carboxylic acid, more particularly a derivative of acetylacetone or of an allyl compound; mention may in particular be made of the acetylacetonato, allyl, cyclopropenyl, carboxylato, carbamato  
30 or dithiocarbamato ligands, more particularly the acetylacetonato and allyl ligands, preferably the acetylacetonato ligand;
- (b) if n is 2,  $\Sigma$  is of the 1-electron radical  
35 ligand X type (according to the definition given in the work Chimie Organométallique referred to above), having a specific behavior in the presence of the iridium atoms; this ligand bridges the 2 iridium

atoms and can be regarded as a 1-electron  
ligand X for 1 iridium atom and as a 3-  
electron ligand LX for the combination of the  
2 iridium atoms; it can in particular be  
5 chosen from halogeno, alkoxy or aryloxy,  
preferably halogeno, more particularly  
chloro, or alkoxy;

2/  $\Sigma'$ , which are identical or different, preferably  
10 identical, each represent a 2-electron ligand L  
(according to the definition given in the work Chimie  
Organométallique referred to above), for example:  
donors of a  $\pi$  bond pair, such as olefins, alkynes, C=O  
double bonds of an aldehyde or of a ketone, C=N or C=S;  
15 donors of a  $\sigma$  bond pair, such as H-H (dihydrogen) bonds  
or H-Si bonds, in particular in silanes (H-SiR<sub>3</sub>); or  
ligands chosen from the following group:  
organophosphorus compounds, R<sub>2</sub>O, R<sub>2</sub>S, NR<sub>3</sub> and THF; the  
organophosphorus ligands are in particular of P(OR)<sub>p</sub>(R)<sub>q</sub>  
20 type with p and q ranging from 0 to 3, it being known  
that p+q = 3, preferably phosphines PR<sub>3</sub> and phosphites  
P(OR)<sub>3</sub> (the R groups are as defined later under -C2-;

the preferred ligands  $\Sigma'$  are hydrocarbon groups  
comprising at least one unit



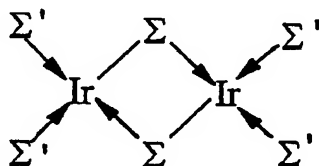
25 those of the latter type being the more preferred, such  
as, for example, cyclooctene;

it may be specified that the hydrocarbon groups  
can be linear, branched, aromatic or (poly)cyclic, can  
30 be optionally interrupted by one or more heteroatoms  
(e.g., O, S or N) and can comprise from 2 to 18 carbon  
atoms; they can be ligands comprising two of these  
units (preferably identical units) capable of bonding  
to the iridium atom (in this case, the two  
35 functionalities  $\Sigma'$  are preferably provided by one and  
the same molecule connected to the iridium via its two

electron-donating functional groups), for example a cyclic compound exhibiting two double bonds, e.g. 1,5-cyclooctadiene, or a diene exhibiting distant double bonds ("distant diene"). Thus, 1,5-cyclo-  
 5 octadiene is a preferred form;

-C2-, on the other hand, a ligand  $\Sigma_d$  chosen from  $R_2S$ ,  $R_2O$ ,  $NR_3$ , carbenes (see, for example, W.A. Herrmann, Angew. Chem. Int. Ed. Engl., 2002, 41, 1290-1309) or  
 10 organophosphorus compounds, in particular of formula  $P(OR)_p(R)_q$  with  $p$  and  $q$  ranging from 0 to 3, it being known that  $p+q = 3$ , preferably phosphines  $PR_3$  and phosphites  $P(OR)_3$ ; in which formulae the  $R$  radicals, which are identical or different, are linear or  
 15 branched alkyl radicals having in particular from 1 to 30 carbon atoms, preferably from 1 to 12 carbon atoms; alkyl radicals comprising one or more rings, in particular 1 or 2 rings, it being possible for a ring to have in particular from 4 to 14 carbon atoms,  
 20 preferably from 5 to 8 carbon atoms; or aryl or aralkyl radicals comprising one or more fused or nonfused aromatic or heteroaromatic rings, in particular 1 or 2 rings, it being possible for a ring to comprise from 4 to 14 carbon atoms, preferably from 5 to 8 carbon  
 25 atoms; the rings can optionally be substituted by one or more groups, in particular from 1 to 2 groups, such as alkoxy, halide, amino or linear or branched alkyl having in particular from 1 to 12 carbon atoms, preferably from 4 to 12 carbon atoms; a phenyl radical,  
 30 optionally substituted as indicated above, may in particular be concerned.

According to a preferred embodiment, the iridium complex is a dimeric complex ( $n = 2$ ) of following formula (I'):



35

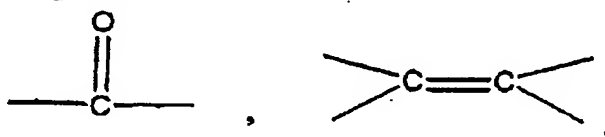
in which  $\Sigma$  and  $\Sigma'$  have the meanings given above,

with the preferences indicated above with regard to the formula (I).

According to a specific embodiment, the catalytic complex -C- is obtained by reaction between:

5 on the one hand, C1a/ a dimeric complex of formula (I') in which:

- $\Sigma$  is a 1-electron radical ligand X chosen from halo, alkoxy or aryloxy, preferably halo, more particularly chloro, or alkoxy;
- 10 -  $\Sigma'$  are 2-electron ligands L formed of hydrocarbon groups comprising at least one unit



preferably of hydrocarbon groups comprising the second unit, more preferably with the two  $\Sigma'$  ligands carried by the same Ir atom being carried by the same molecule, e.g. 1,5-cyclooctadiene, and, on the other hand, C2a/ a ligand  $\Sigma_a$  chosen from  $R_2S$ ,  $R_2O$ ,  $NR_3$ , carbenes and more particularly organo-phosphorus compounds, in particular of formula 15  $P(OR)_p(R)_q$  with p and q ranging from 0 to 3, it being known that  $p+q = 3$ , preferably phosphines  $PR_3$  and phosphites  $P(OR)_3$ , with R as defined above, in particular R representing identical or different, preferably identical, aryl or aralkyl groups comprising 20 one or more fused or nonfused aromatic or hetero-aromatic rings, in particular 1 or 2 rings; it being possible for a ring to comprise from 4 to 14 carbon atoms, preferably from 5 to 8 carbon atoms, e.g. phenyl. This or these rings can be substituted by one 25 or more groups, such as alkoxy, halide, amino and linear or branched alkyl, as seen above.

According to a preferred embodiment, the dimeric iridium complex (I') is bis(1,5-cyclooctadiene)di-iridium(I) dichloride of formula  $[IrCl(cycloocta-$  35  $diene)]_2$ . It is a commercial product.

According to a preferred embodiment, the ligand  $\Sigma_a$



is triphenylphosphine (TPP). By way of example, mention may also be made of tris(para-methoxyphenyl)phosphine.

According to a preferred embodiment, the catalytic complex -C- is the product of the mixing of bis(1,5-cyclooctadiene)diiridium(I) dichloride and of TPP.

As indicated below, the catalytic complex -C- is preferably obtained by reacting the abovementioned entities at ambient temperature, e.g. in the vicinity of 25°C, and in the open air, optionally in the presence of a solvent which makes it possible, if necessary, to dissolve the reactive entities. It is clearly understood that different reaction conditions can be applied in an equivalent way so as to obtain a conforming catalytic complex.

The use of such a catalytic complex -C- makes it possible to efficiently catalyze the dehydrogenative condensation reaction between  $\equiv\text{SiH}$  and  $\equiv\text{SiOH}$  siloxane entities under mild temperature conditions, generally at temperatures of less than 150°C, in particular of less than 100°C, and optionally at ambient temperature. Silicone networks or polymers are thus obtained in a few minutes, with variable  $\equiv\text{SiH}/\equiv\text{SiOH}$  ratios.

The catalytic complexes carefully selected in accordance with the invention are effective and economic, in particular with regard to platinum-based catalysts.

It is very simple to test various iridium complex/ligand  $\Sigma_a$  pairs and to observe their properties and behavior. As is illustrated in the examples part, the preparation of the catalytic complex does not require a complex process or critical operating conditions. It is sufficient, for example, to prepare a mixture of an iridium complex and of a ligand  $\Sigma_a$  to be tested, optionally to dissolve this mixture in a solvent, such as toluene, in the case where the starting entities are in solid form, then to mix the combined product with a silicone composition comprising at least one POS A and one POS B according to the invention and optionally a crosslinking retarder, and

to observe the crosslinking time at ambient temperature and/or at a higher temperature, e.g. under temperature conditions similar to the practical application desired. Phosphites and phosphines are, for example, chemical entities which are widely available. It is possible in particular to test combinations of ligands  $\Sigma_d$  and of iridium complexes which are commercially available, such as phosphites and phosphines and bis(1,5-cyclooctadiene)diiridium dichloride and (1,5-cyclooctadiene)(acetylacetonato)iridium. The incorporation, in the preparation of the silicone composition, of a simple stage for the preparation of the catalytic complex thus exhibits very obvious advantages, including the possibility of having available varied catalytic complexes suited to the circumstances (e.g., suited to the crosslinking duration and temperature conditions).

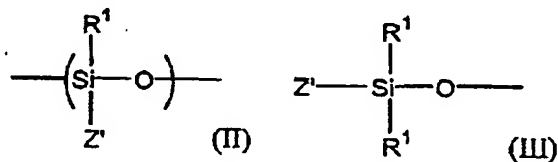
These catalytic complexes are in particular advantageous in preparing the elastomeric silicone networks under mild and economical conditions. The applications targeted in this case relate in particular to the adhesion resistance of paper, where it is desired to replace the current systems by less expensive systems, and silicone foams, where it is desired to control the evolution of hydrogen and the quality of the network. For the first application, it is preferable to control the diffusion of the hydrogen in order to prevent the formation of bubbles. For the second application, it is necessary to manage the size of the bubbles in order to optimize the properties of the final foam. These results are all the more significant as the reactivity of siloxane entities, in particular in forming nonlinear (crosslinked) products, is not very high if it is compared with that of hydrosilanes and alcohols in dehydrogenative condensation.

Quantitatively, use is made of 1 ppm to 1000 ppm, in particular of 1 ppm to 300 ppm, of iridium metal with respect to the body composed of the mixture of the

oils possessing  $\equiv\text{SiH}$  and  $\equiv\text{SiOH}$ . When the present patent application deals with ranges, the limits are included.

The catalytic complex employs in particular from 0.5 to 10, especially from 0.5 to 5, more particularly from 0.5 to 2, mol of ligand  $\Sigma_d$  per 1 mol of Ir. Depending on the preferred embodiment of the invention, use is made of 0.75 to 1.5, in particular of 0.75 to 1.25 and better still of 1 mol of ligand  $\Sigma_d$  per 1 mol of Ir.

The siloxane entity -A- comprising reactive  $\equiv\text{SiH}$  units is preferably chosen from the entities which have at least one unit of formula (II) and which are terminated by units of formula (III) or from the cyclic entities (generally comprising from 3 to 12 Si atoms) composed of units of formula (II), these formulae being represented below:



in which:

- the symbols  $\text{R}^1$  are identical or different and represent:
  - a linear or branched alkyl radical comprising from 1 to 8 carbon atoms which is optionally substituted by at least one halogen, preferably fluorine, the alkyl radicals preferably being methyl, ethyl, propyl, octyl and 3,3,3-trifluoropropyl,
  - an optionally substituted cycloalkyl radical comprising between 5 and 8 cyclic carbon atoms,
  - an optionally substituted aryl radical comprising between 6 and 12 carbon atoms,
  - an aralkyl radical having an alkyl part comprising between 5 and 14 carbon atoms and an aryl part comprising between 6 and 12 carbon atoms which is optionally

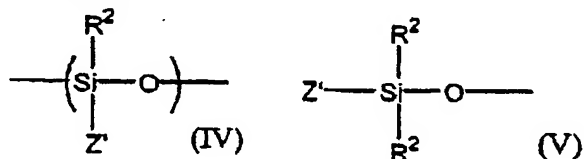
substituted on the aryl part by halogens,  
alkyls and/or alkoxyis comprising from 1 to  
3 carbon atoms,

5       - the symbols Z are alike or different and  
      represent:

- H,
- a group corresponding to the same definition  
as that given above for R<sup>1</sup>,

10       with, per molecule, at least one of the symbols Z  
      representing H.

      As regards the siloxane entities -B- comprising  
reactive ≡SiOH units, the selection is made in  
particular in the context of the invention of those  
which have at least one unit of formula (IV) and which  
15       are terminated by units of formula (V) or of cyclic  
      entities (generally comprising from 3 to 12 Si atoms)  
      which are composed of units of formula (IV), these  
      formulae being represented below:



20       in which:

      - the symbols R<sup>2</sup> are identical or different and  
      represent:

- a linear or branched alkyl radical comprising  
from 1 to 8 carbon atoms which is optionally  
25       substituted by at least one halogen,  
      preferably fluorine, the alkyl radicals  
      preferably being methyl, ethyl, propyl, octyl  
      and 3,3,3-trifluoropropyl,
- an optionally substituted cycloalkyl radical  
30       comprising between 5 and 8 cyclic carbon  
      atoms,
- an optionally substituted aryl radical  
      comprising between 6 and 12 carbon atoms,
- an aralkyl radical having an alkyl part  
35       comprising between 5 and 14 carbon atoms and

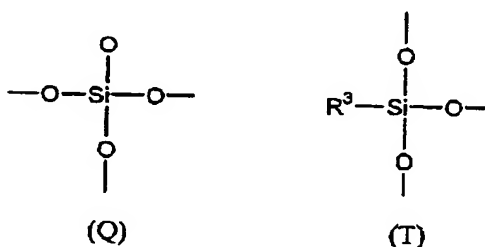
an aryl part comprising between 6 and 12 carbon atoms which is optionally substituted on the aryl part by halogens, alkyls and/or alkoxyis comprising from 1 to 3 carbon atoms,

5 - the symbols  $Z'$  are alike or different and represent:

- a hydroxyl group,
- a group corresponding to the same definition as that given above for  $R^2$ ,

10 with, per molecule, at least one of the symbols  $Z'$  representing OH.

The entities of -A- and -B- type can also include, in their structure, "Q" or "T" units defined as indicated below:

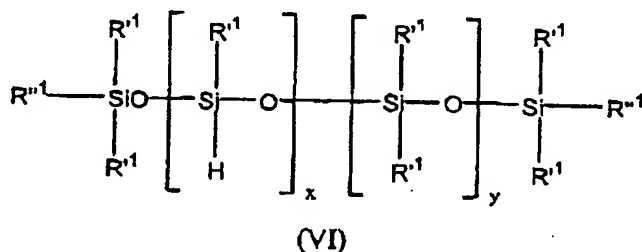


with it being possible for  $R^3$  to represent one of the substituents provided for  $R^1$  or  $R^2$ .

20 According to an advantageous embodiment of the invention, the polyorganosiloxanes -A- used comprise from 1 to 50 SiH units per molecule.

According to an advantageous embodiment of the invention, the polyorganosiloxanes -B- used comprise from 1 to 50 SiOH units per molecule.

25 According to a preferred embodiment, the polyorganosiloxanes -A- correspond to the general formula (VI):

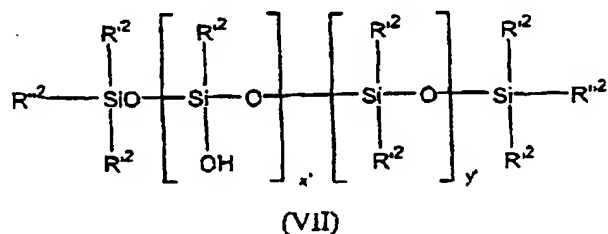


in which:

- x and y each represent an integer or fractional number varying between 0 and 200,
- R<sup>'1</sup> and R<sup>"1</sup> represent, independently of one another:

- 5 • a linear or branched alkyl radical comprising from 1 to 8 carbon atoms which is optionally substituted by at least one halogen, preferably fluorine, the alkyl radicals preferably being methyl, ethyl, propyl, octyl
- 10 and 3,3,3-trifluoropropyl,
- an optionally substituted cycloalkyl radical comprising between 5 and 8 cyclic carbon atoms,
- an optionally substituted aryl radical
- 15 comprising between 6 and 12 carbon atoms,
- an aralkyl radical having an alkyl part comprising between 5 and 14 carbon atoms and an aryl part comprising between 6 and 12 carbon atoms which is optionally
- 20 substituted on the aryl part,
- it being possible for R<sup>"1</sup> also to correspond to hydrogen, with the condition according to which at least one of the R<sup>"1</sup> radicals (preferably both) correspond to hydrogen when x = 0.

25 According to a preferred embodiment, the poly-organosiloxanes -B- correspond to the general formula (VII):



in which:

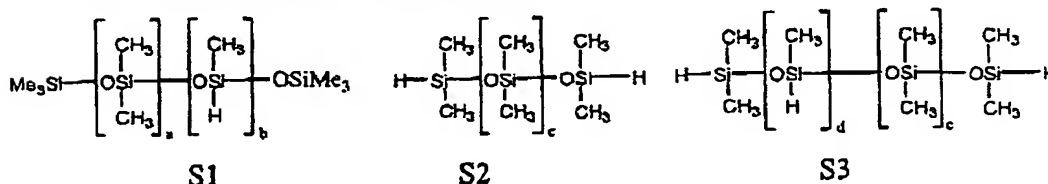
- 30 - x' and y' each represent an integer or fractional number varying between 0 and 1200,
- R<sup>'2</sup> and R<sup>"2</sup> represent, independently of one another:
- a linear or branched alkyl radical comprising

from 1 to 8 carbon atoms which is optionally substituted by at least one halogen, preferably fluorine, the alkyl radicals preferably being methyl, ethyl, propyl, octyl and 3,3,3-trifluoropropyl,

- an optionally substituted cycloalkyl radical comprising between 5 and 8 cyclic carbon atoms,
- an optionally substituted aryl radical comprising between 6 and 12 carbon atoms,
- an aralkyl radical having an alkyl part comprising between 5 and 14 carbon atoms and an aryl part comprising between 6 and 12 carbon atoms which is optionally substituted,

- it being possible for  $R''^2$  also to correspond to OH, with the condition according to which at least one of the  $R''^2$  radicals (preferably both) correspond to OH when  $x' = 0$ .

The following compounds:



with a, b, c, d and e representing a number varying from:

- in the polymer of formula S1:

0 ≤ a ≤ 150, preferably 0 ≤ a ≤ 100, preferably 0 ≤ a ≤ 20, and

1 ≤ b ≤ 55, preferably 10 ≤ b ≤ 55, preferably 30 ≤ b ≤ 55,

- in the polymer of formula S2:

0 ≤ c ≤ 15,

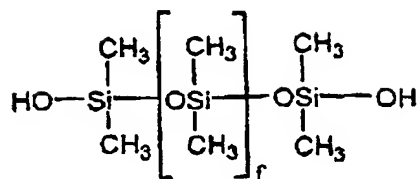
- in the polymer of formula S3:

5 ≤ d ≤ 200, preferably 20 ≤ d ≤ 50, and

2 ≤ e ≤ 50, preferably 10 ≤ e ≤ 30,

are very particularly suitable in the invention as polyorganosiloxanes -A-.

The compounds of formula:



S4

with  $1 \leq f \leq 1200$ , preferably  $50 \leq f \leq 400$  and more preferably still  $150 \leq f \leq 250$ ,

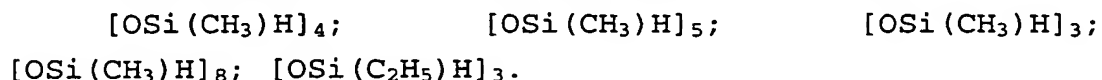
5 are very particularly suitable in the invention as polyorganosiloxanes -B-.

Provided that the siloxane entities -A- and -B- are oligomers or polymers, they can be described as indicated below.

10 The POS -A- can be linear (e.g. (VI)), branched or cyclic. For economic reasons, its viscosity is preferably less than 100 mPa·s at 25°C; the identical or different organic radicals are preferably methyl, ethyl and/or phenyl. When the POS is linear, the  
15 hydrogen atoms of the  $\equiv\text{SiH}$  functional groups are bonded directly to the silicon atoms situated at the chain end(s) and/or in the chain.

Mention may be made, as example of linear constituent -A-, of polymethylhydrosiloxanes comprising  
20 trimethylsiloxyl and/or hydrodimethylsiloxyl ends.

Mention may be made, among cyclic polymers, of those corresponding to the following formulae:



25 Mention may be made, as concrete examples of branched polymers, of:

$\text{CH}_3\text{Si}[\text{CH}_3]_3[\text{OSi}(\text{CH}_3)_2\text{H}]_2$ ;  $\text{Si}[\text{OSi}(\text{CH}_3)(\text{C}_2\text{H}_5)\text{H}][\text{OSi}(\text{CH}_3)_2\text{H}]_3$   
and those composed of  $\text{SiOH}_2$  units and  $\text{H}(\text{CH}_3)_2\text{SiO}_{0.5}$  units with a  $\text{CH}_3\text{Si}$  ratio of 1 to 1.5.

30 The constituent -B- can exhibit a viscosity which can reach 200 000 mPa·s. For economic reasons, a constituent having a viscosity generally of the order of 20 to 10 000 mPa·s is chosen.

The identical or different organic groups



generally present in the  $\alpha,\omega$ -hydroxylated oils or gums are the methyl, ethyl, phenyl or trifluoropropyl radicals. Preferably, at least 80% by number of said organic groups are methyl groups bonded directly to the silicon atoms. In the context of the present invention, preference is given more especially to  $\alpha,\omega$ -bis(hydroxy)polydimethylsiloxanes.

The -B- entities can comprise resins possessing silanol functional groups exhibiting, per molecule, at least one of the  $R'SiO_{0.5}$  unit (M unit) and  $R'^2SiO$  unit (D unit), in combination with at least one of the  $R'SiO_{0.5}$  unit (T unit) and  $SiO_2$  unit (Q unit). The  $R'$  radicals generally present are methyl, ethyl, isopropyl, tert-butyl and n-hexyl. Mention may be made, as examples of resins, of the resins MQ(OH), MDQ(OH), TD(OH) and MDT(OH).

It is possible to employ solvents for the POS -A- or -B-, so as to adjust the viscosity of the composition. Mention may be made, as examples of such conventional solvents for silicone polymers, of solvents of aromatic type, such as xylene and toluene, saturated aliphatic solvents, such as hexane, heptane, White Spirit®, tetrahydrofuran and diethyl ether, or chlorinated solvents, such as methylene chloride and perchloroethylene. In the context of the present invention, it will be preferable, however, not to use a solvent.

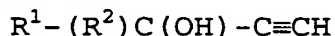
The respective amounts of siloxane entities -A- and -B- are also determining in order to be able to satisfactorily carry out the dehydrogenative condensation of the composition according to the invention.

Thus, the  $\equiv SiH/\equiv SiOH$  ratio is advantageously between 1 and 100, preferably between 2 and 50 and more preferably still between 2 and 25.

The composition according to the invention can also comprise at least one crosslinking inhibitor or retarder -D-. Such a constituent is generally used to confer a degree of pot life on the ready-for-use

composition. By varying, on the one hand, the nature of the catalytic combination and its concentration in the composition (which results in a given crosslinking rate) and, on the other hand, the nature of the retarder and its concentration, it is possible to adjust the pot life. The activity of the catalytic combination is restored by heating (thermal activation). The retarder is preferably chosen from acetylenic alcohols (ethynylcyclohexanol: ECH) and/or diallyl maleates and/or triallyl isocyanurates and/or dialkyl maleates (diethyl maleates) and/or dialkyl alkynedicarboxylates (diethyl acetylenedicarboxylate) or alternatively from polyorganosiloxanes, advantageously cyclic and substituted by at least one alkenyl, tetramethylvinylcyclotetrasiloxane being particularly preferred, or alkylated maleates.

Acetylenic alcohols (see, for example, FR-B-1 528 464 and FR-A-2 372 874) are the preferred retarders. They are in particular those corresponding to the following formula:



in which:

.  $R^1$  is a linear or branched alkyl radical or a phenyl radical;

25 .  $R^2$  is H or a linear or branched alkyl radical or a phenyl radical;

it being possible for the  $R^1$  and  $R^2$  radicals and the carbon atom situated in the alpha position with respect to the triple bond optionally to form a ring;

30 the total number of carbon atoms present in  $R^1$  and  $R^2$  being at least 5, preferably from 9 to 20.

Said alcohols are preferably chosen from those exhibiting a boiling point of greater than 250°C. Mention may be made, as examples, of:

- 35 . 1-ethynylcyclohexan-1-ol;  
  . 3-methyldodec-1-yn-3-ol;  
  . 3,7,11-trimethyldodec-1-yn-3-ol;  
  . 1,1-diphenylprop-2-yn-1-ol;  
  . 3-ethyl-6-ethylnon-1-yn-3-ol;

. 3-methylpentadec-1-yn-3-ol.

These  $\alpha$ -acetylenic alcohols are commercial products.

Such a retarder is present in particular in a proportion of 3000 ppm at most, preferably in a proportion of 100 to 2000 ppm, with respect to the total weight of the compounds -A- and -B-.

The composition according to the invention can also comprise one or more POS resins -E-. These resins are well known branched POS oligomers or polymers which are commercially available. They are present in the form of solutions, preferably siloxane solutions. They exhibit, in their structure, at least two different units chosen from those of formula  $R^*_3SiO_{0.5}$  (M unit),  $R^*_2SiO$  (D unit),  $R^*SiO_{1.5}$  (T unit) and  $SiO_2$  (Q unit), at least one of these units being a T or Q unit.

The  $R^*$  radicals are identical or different and are chosen from linear or branched  $C_1$ - $C_6$  alkyl radicals,  $C_2$ - $C_4$  alkenyl radicals, the phenyl radical or the 3,3,3-trifluoropropyl radical. Mention may be made, for example, as  $R^*$  alkyl radicals, of the methyl, ethyl, isopropyl, tert-butyl and n-hexyl radicals and, as  $R^*$  alkenyl radicals, of the vinyl radical. It should be understood that, in the POS resins -E- of the abovementioned type, for a portion of them, the  $R^*$  radicals are alkenyl radicals.

Mention may be made, as examples of branched organopolysiloxane oligomers or polymers -E-, of MQ resins, MDQ resins, TD resins and MDT resins, it being possible for the alkenyl functional groups to be carried by the M, D and/or T units. Mention may be made, as examples of resins -E- which are particularly well suited, of the vinylated MDQ or MQ resins having a content by weight of vinyl groups of between 0.2 and 10% by weight, these vinyl groups being carried by the M and/or D units.

This structuring resin -E- is advantageously present in a concentration of between 10 and 70% by weight with respect to the combined constituents of the

composition, preferably between 30 and 60% by weight and more preferably still between 40 and 60% by weight.

The composition according to the invention can also comprise a filler -F-, preferably an inorganic  
5 filler, chosen from siliceous or nonsiliceous materials.

When siliceous materials are concerned, they can act as reinforcing or semi-reinforcing filler. The reinforcing siliceous fillers are preferably chosen  
10 from colloidal silicas, fumed and precipitated silica powders, or their mixtures. Semi-reinforcing siliceous fillers, such as diatomaceous earths or ground quartz, can also be employed. These powders exhibit a main particle size generally of less than  $0.1 \mu\text{m}$  and a  
15 specific surface BET of greater than  $50 \text{ m}^2/\text{g}$ , preferably between 100 and  $300 \text{ m}^2/\text{g}$ .

As regards nonsiliceous organic materials, they can be involved as semi-reinforcing or bulking inorganic filler. Examples of these nonsiliceous  
20 fillers, which can be used alone or as a mixture, are carbon black, titanium dioxide, aluminum oxide, alumina hydrate, expanded vermiculite, zirconia, a zirconate, unexpanded vermiculite, calcium carbonate, zinc oxide, mica, talc, iron oxide, barium sulfate and slaked lime.  
25 These fillers have a particle size generally of between  $0.001$  and  $300 \mu\text{m}$  and a BET specific surface of less than  $100 \text{ m}^2/\text{g}$ .

In practice but without implied limitation, the filler employed is a silica.

30 The filler can be treated using any appropriate compatibilizing agent and in particular hexamethyldi-silazane. For further details in this regard, reference may be made, for example, to patent FR-B-2 764 894.

With regard to the weight, it is preferable to  
35 employ an amount of filler of between 5 and 30%, preferably between 7 and 20%, by weight, with respect to the combined constituents of the preparation.

Naturally, the composition can be enriched using all kinds of additives, depending upon the final

applications targeted.

In the adhesion resistance application on flexible supports (paper or polymer film), the composition can comprise an adhesion adjusting system selected from known systems. Those disclosed in French patent FR-B-2 450 642, patent US-B-3 772 247 or European patent application EP-A-0 601 938 may be concerned. Mention may be made, as examples, of the adjusting systems based:

- o on 96 to 85 parts by weight of at least one reactive polyorganosiloxane resin (A) of type:  $MD^{Vi}Q$ ,  $MM^{Vi}Q$ ,  $MD^{Vi}T$ ,  $MM^{hexenyl}Q$  or  $MM^{allyloxypropyl}Q$ ,
- o on 4 to 15 parts by weight of at least one unreactive resin (B) of type:  $MD'Q$ ,  $MDD'Q$ ,  $MDT'$ ,  $MQ$  or  $MDQ$ .

Other functional additives of this composition can be stabilizing agents, bactericides, photosensitizers, fungicides, corrosion inhibitors, antifreeze agents, wetting agents, antifoaming agents, synthetic latexes, colorants or acidifying agents.

Mention may also be made, among conventional additives, of adhesion promoters, such as, for example, those comprising at least one alkoxyated organosilane, at least one epoxidized organosilicon compound and at least one metal chelate and/or one metal alkoxide, for example VTMO (VinylTriMethoxySilane), GLYMO (GLYcidoxypropyltriMethOxysilane) or TBT (tert-butyl titanate).

This composition can be a solution or an emulsion. In the latter case, it can then comprise at least one surfactant and optionally at least one agent for fixing the pH, such as  $HCO_3^-/CO_3^{2-}$  and/or  $H_2PO_4^-/HPO_4^{2-}$ .

Another subject matter of the present invention is the use of a catalytic iridium complex as defined in the present application as dehydrogenative condensation catalyst for a silicone composition which crosslinks by dehydrogenative condensation, this composition being moreover defined in the present application.

A further subject matter of the present invention

is the catalytic complexes capable of being obtained in accordance with the invention by reacting at least one iridium complex as defined above and at least one ligand as defined above.

5       According to yet another of its aspects, the present invention relates to a process for polymerizing and/or crosslinking a composition as defined above. This process is characterized in that a dehydrogenative condensation is carried out between said compounds -A-  
10       and -B- and in that said dehydrogenative condensation is initiated by thermal activation of the catalytic complex -C-. The catalytic complex according to the invention can be prepared in a first stage by mixing the abovementioned entities, as described above.

15       According to another alternative form of the invention, the invention relates to a process for the preparation of a branched polyorganosiloxane comprising at least two polyorganosiloxane chains connected to one another via an Si-O-Si siloxyl group in which a  
20       dehydrogenative condensation reaction is carried out between an organosiloxane monomer, oligomer or polymer A' comprising reactive  $\equiv\text{SiH}$  units and an organosiloxane monomer, oligomer or polymer B' comprising reactive  $\equiv\text{SiOH}$  units, characterized in that said dehydrogenative  
25       condensation reaction is carried out in the presence of the catalytic complex C defined as above or according to one of claims 1 to 15 and is optionally initiated by thermal activation. According to a preferred form, the  $\equiv\text{SiH}/\equiv\text{SiOH}$  ratio is greater than 1.

30       The catalytic complex can either be added to the mixture of the compounds A and B, for example of the polymers of the S1 or S2 or S3 type with a polymer of the S4 type, or, preferably, be mixed beforehand with the compound B, for example the polymer of the S4 type,  
35       before being brought into contact with the compound A, for example the polymer S1 or S2 or S3. Generally, the mixtures are prepared with stirring at ambient temperature.

The catalytic complex can be employed as is or in

solution in a solvent.

The catalytic complex solution can, for example, be used to prepare a bath with the monomer(s), oligomer(s) and/or polymer(s) to be polymerized and/or crosslinked by dehydrogenative condensation, so that the concentration of the catalytic complex(es) present is between 0.01 and 5% by weight in said bath and preferably between 0.05 and 0.5%.

The solvents which can be used can in particular be esters, ethers, aromatic solvents, water in the form of traces, carbonates and hindered alcohols. Mention may be made, for the alcohols, of isopropylbenzyl alcohol or benzyl alcohol. Mention may be made, for the ethers, of di(n-butyl) ether. Mention may be made, for the esters, of dibutyl maleate, dimethyl ethylmalonate, methyl salicylate, dioctyl adipate, butyl tartrate, ethyl lactate, n-butyl lactate or isopropyl lactate. Other solvents are toluene and tetrahydrofuran.

The silicone composition according to the invention, which can be used in particular as coating base for the preparation of release coatings possessing a water-repellant nature, is prepared using means and according to mixing methodologies well known to a person skilled in the art, whether compositions, with or without solvents, or emulsions are involved.

The invention also relates to a process for producing at least one release coating on a support, preferably a flexible support, characterized in that it comprises the application, to this support, of a composition as defined above, preferably employing POS -A- and -B- as defined above, and then ensuring that crosslinking occurs.

In accordance with this process, the compositions can be applied using devices used on industrial machines for coating paper, such as a roll coating head, e.g. a five-roll coating head, or air knife or smoothing rod systems, on flexible supports or materials and then cured by moving through appropriate heating devices, such as tunnel ovens heated at 70-

200°C; the passage time in these ovens depends on temperature; it is generally of the order of 5 to 15 seconds at a temperature of the order of 100°C and of the order of 1.5 to 3 seconds at a temperature of the order of 180°C.

Said compositions can be deposited on any flexible material or substrate, such as paper of various types (e.g., supercalendered, coated or glassine), board, cellulose sheets, metal sheets or plastic films (polyester, polyethylene, polypropylene, and the like).

The amounts of compositions deposited can be of the order of 0.5 to 2 g per m<sup>2</sup> of surface to be treated, which corresponds to the deposition of layers of the order of 0.5 to 2 μm.

The materials or supports thus coated can subsequently be brought into contact with any adhesive material, e.g. rubber, acrylic or other, which is sensitive to pressure. The adhesive material is then easily detachable from said support or material.

The flexible supports coated with a release silicone film can, for example, be:

- an adhesive tape, the internal face of which is coated with a layer of pressure-sensitive adhesive and the external face of which comprises the release silicone coating;
- or a paper or a polymer film for protecting the adhesive face of a self-adhesive or pressure-sensitive adhesive element;
- or a polymer film of the poly(vinyl chloride) (PVC), polypropylene, polyethylene or poly(ethylene terephthalate) type.

Another subject matter of the invention is a process for producing at least one article made of crosslinked silicone foam, characterized in that it comprises the stage of crosslinking a composition as defined above, while preferably employing the POS A and POS B as defined above, while ensuring that at least a portion of the hydrogen gas formed is not discharged from the reaction medium.



The compositions according to the invention are of use in the field of release coatings on paints, the encapsulation of electrical and electronic components, or coatings for textiles, and in the field of the sheathing of optical fibers.

Another subject matter of the invention is any coating obtained by crosslinking a composition comprising siloxane entities -A- possessing reactive SiH units, e.g. of S1, S2 or S3 type, as are defined above, and siloxane entities -B-, e.g. of S4 type, as are defined above. These coatings can be of varnish, adhesive coating, release coating and/or ink type.

The invention is also targeted at:

- any article composed of a solid material, at least one surface of which is coated with the composition targeted above which is thermally polymerized and/or crosslinked;
- and the crosslinked silicone foam, in particular a foam obtained by crosslinking a composition comprising the entities S1 and/or S2 and/or S3 as components -A- and the entity of S4 type as components -B-, with production of hydrogen gas by dehydrogenative condensation.

Another subject matter of the present invention is the resins or polymers capable of being obtained from the compositions described above.

The invention will now be described in more detail using nonlimiting implementational examples.

#### EXAMPLES

##### Examples 1 to 10 and counter example 1

##### General procedure for examples 1 to 10:

A mixture of silicone oils is prepared from the following reactive oils:

- a polymethylhydrosiloxane oil comprising 1600 meq. SiH/100 g and having a viscosity of 30 mPa·s, hereinafter SiH oil,
- an  $\alpha,\omega$ -dihydroxylated polydimethylsiloxane oil comprising 14 meq. SiOH/100 g and having a

viscosity of 750 mPa·s, hereinafter SiOH oil.

Furthermore, the desired amounts of iridium complex  $[\text{IrClCod}]_2$  and of ligand  $\Sigma_4$  are weighed out in a 30 ml flask equipped with a magnetic stirrer and are then diluted with a small amount of sulfur-free toluene (0.5 ml). The necessary amount of the preformed mixture of silicone oils is added to this solution. The time measurements begin at this point, at the same time as the magnetic stirring begins.

After stirring at ambient temperature, the setting (crosslinking) time is measured. The conditions and the results are combined in table 1.

#### General procedure for counter example 1

A mixture of silicone oils is prepared from the following reactive oils:

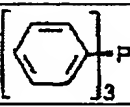
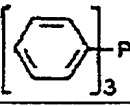
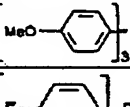
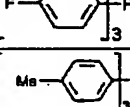
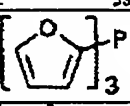
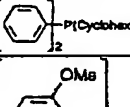
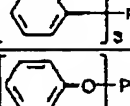
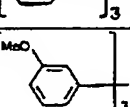
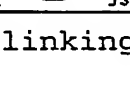
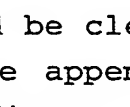
- a polymethylhydrosiloxane oil comprising 1600 meq. SiH/100 g and having a viscosity of 30 mPa·s, hereinafter SiH oil,
- an  $\alpha,\omega$ -dihydroxylated polydimethylsiloxane oil comprising 14 meq. SiOH/100 g and having a viscosity of 750 mPa·s, hereinafter SiOH oil.

Furthermore, the desired amounts of iridium complex  $[\text{IrClCod}]_2$  are weighed out in a 30 ml flask equipped with a magnetic stirrer and are then diluted with a small amount of sulfur-free toluene (0.5 ml). After stirring for 10 minutes, the necessary amount of the preformed mixture of silicone oils is added to this solution. The time measurements begin at this point, at the same time as the magnetic stirring begins.

After stirring at ambient temperature, the setting (crosslinking) time is measured.

The conditions and the result are combined in table 1.

**TABLE 1 - RESULTS**

	[IrClCod] <sub>2</sub> (mg)	Ligand $\Sigma_d$		SiOH oil (g)	SiH oil (g)	Molar ratio			Cross- linking Ambient temp.
		Nature	(mg)			$\Sigma_d$ /Ir	SiH/ SiOH	Ir/ SiOH	
Counter ex. 1	2.2	-	0	11.1	0.19	-	2	$4.2 \times 10^{-3}$	NC*
ex. 1	4.7		3.8	23.5	0.4	1	2	$4.2 \times 10^{-3}$	2 min
ex. 2	3.5		5.6	17.5	0.3	2	2	$4.2 \times 10^{-3}$	1 h
ex. 3	5		4.3	25	0.43	1	2	$4.2 \times 10^{-3}$	2 min
ex. 4	4.8		4.3	24	0.41	1	2	$4.2 \times 10^{-3}$	2 min
ex. 5	3.9		3.5	19.5	0.34	1	2	$4.2 \times 10^{-3}$	4 min
ex. 6	3.4		2.5	17	0.29	1.1	2	$4.2 \times 10^{-3}$	7 min
ex. 7	3.5		2.7	17.5	0.3	1	2	$4.2 \times 10^{-3}$	7 min
ex. 8	4		4.0	20	0.34	1	2	$4.2 \times 10^{-3}$	12 min
ex. 9	3.5		3.0	17.5	0.3	1	2	$4.2 \times 10^{-3}$	18 min
ex. 10	3.5		3.5	17.5	0.3	1	2	$4.2 \times 10^{-3}$	3 min

\* NC: No crosslinking after stirring at a.t. for 6 h

5           It should be clearly understood that the invention  
defined by the appended claims is not limited to the  
specific embodiments indicated in the description above  
but encompasses the alternative forms thereof which  
depart neither from the scope nor from the spirit of  
10   the present invention.